Low-frequency Raman scattering for water-ethanol binary mixtures

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Low-frequency Raman scattering for water-ethanol binary mixtures

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水・エタノール二成分混合系について室温で低振動ラマン散乱スペクトルを測定し、低濃度を重点的に詳細な濃度依存性を調べた。低濃度において 180cm^{-1} のモードの動的感受率の虚部が大きく減少していることが分かった。

1. Introduction

In aqueous solution and water binary mixture, homogeneity or dynamical structures have been reported[1-3], but the detail is not clear. Using low frequency Raman scattering, the information of the intermolecular vibration can be obtained. For water and ethanol binary mixtures, the imaginary part of dynamical susceptibility spectra $\chi''(\nu)$of mixtures can be decomposed into linear combination of pure water and neat ethanol in the frequency range 40 - 250 cm^{-1} in the right angle geometry. Below 40 cm^{-1}, there are deviation from the combination of the spectra of pure components and observed spectra. [2] In this report, it is shown that the results of the detail concentration dependence with the low frequency Raman scattering up to around the inflection point, ethanol 20 mol%.

2. Experimental

Low-frequency Raman scattering spectra were obtained using a triple-grating spectrometer of additive dispersion (Jobin-Yvon T64000) with a YAG laser operated 532 nm with power of 300 mW at room temperature. Depolarized spectra were recorded in the frequency range from 10 to 600 cm^{-1} and resolution was 3 cm^{-1} in the back scattering geometry. Pure water and ethanol (purity more than 99.9 %) were used for the preparation of the samples.

3. Results and Discussion

The intensity of Raman spectra $I(\nu)$ was reduced into $\chi''(\nu)$ using following equation,

$$\chi''(\nu) = K(\nu_i - \nu)^{-4}[n(\nu)+1]^{-1} I(\nu), \qquad (1)$$

where K is the instrument constant, ν_i is the frequency of incident light and ν is the Raman shift in cm^{-1}. $n(\nu) = [\exp(hc\nu/kT)-1]^{-1}$ is the Bose-Einstein factor, c is the velocity of light and T is the absolute temperature. Figure 1 (a) shows the reduced spectra of the variation of the concentration from ethanol concentration 0 mol% (water) to 100 (ethanol) and the isosbestic point is found around 125 cm^{-1}, which is very close to the value reported before.[1,2] Two broad bands around 50 and 180 cm^{-1} in the pure water spectra were assigned to the O-O-O bending motion of hydrogen bonded trimer unit and O-O stretching motion of hydrogen bonds, respectively.[1] It is seen in Fig. 1(a),(b) that the behaviors of the two broad bands are different in the changes of the profile of bands with the increase of ethanol. Figure 1(b) shows the reduced spectra in the concentration range from 0 to 8 mol%. $\chi''(\nu)$ of the band of 50 cm^{-1} slightly changes, while that of 180 cm^{-1} changes markedly. From this result, we can conclude that the O-O-O bending motion of hydrogen bonded does not change remarkedly up to around 8 mol% whereas the O-O

stretching motion of hydrogen bond changes markedly.

$\chi''(\nu)$ spectra of mixtures were decomposed into the combination of pure water and neat ethanol in the frequency range of 150 - 600 cm^{-1} in the back scattering geometry. The decomposition was done in the wide frequency range including the mode of vibration of ethanol molecule at 435 cm^{-1}.The coefficients of the spectra of pure water and neat ethanol were determined and the concentration dependence of coefficients of water and ethanol is shown in Fig. 2 using $\chi''(\nu)= A\chi''_{water}(\nu) + B\chi''_{ethanol}(\nu)$. It is found that both coefficients change linearly with the increase of the ethanol up to 20 mol%, however, above 20 mol% does not change linearly.

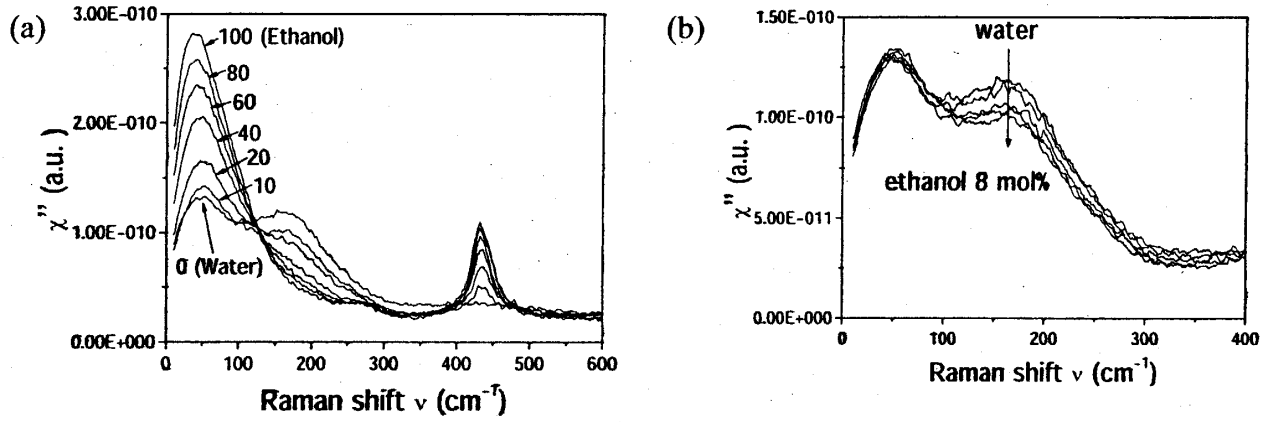

Figure 1. The concentration dependence of water-ethanol spectra. (a) ethanol concentration 0 (water), 10, 20, 40, 60, 80, 100 mol% (ethanol). (b) ethanol concentration 0 (water), 2, 4, 6, 8 mol%.

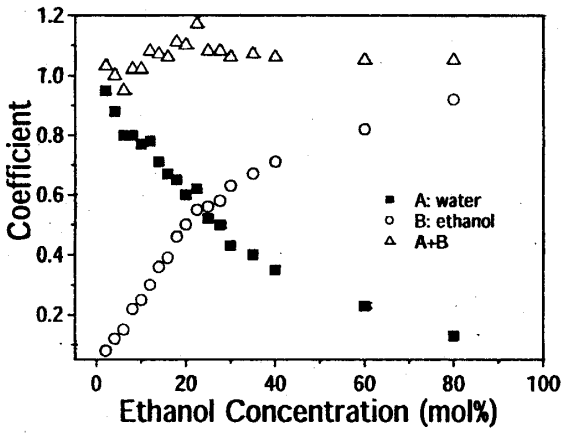

Figure 2. The coefficients of components as a function of ethanol concentration.

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